

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of: **R. Singh, et al.**

Examiner: **A. Khan**

Application No.: **10/694,273**

Group Art Unit: **1751**

Filed: **October 27, 2003**

Docket No.: **H0003965-4510**

Title: **COMPOSITIONS CONTAINING FLUORINE SUBSTITUTED OLEFINS**

Commissioner for Patents  
Alexandria, VA 22313-1450

**RULE 132 DECLARATION OF RAJIV SINGH**

I, Rajiv Singh, declare and state that:

1. I am a co-inventor in the above-mentioned patent application. I hold a Ph. D. degree in Chemistry from University of Tennessee (1987). I have been employed by Honeywell International, Inc., for 19 years, holding various positions including Research Chemist. I am currently a Senior Fellow. I have extensive experience in the production and application of compounds and compositions for use in refrigeration processes.

2. I have reviewed and am familiar with information contained in JP04110388 – Daikin (hereinafter “Daikin”) as a result of reviewing the English language translation thereof, which is attached hereto as Exhibit A. The Daikin reference discloses generally the use of fluorinated propenes as refrigerants. The materials disclosed for use in Daikin are fluorinated propenes having a degree of

fluorination ranging from mono-fluorination to penta-fluorination. This general disclosure encompasses thirty possible compounds when all geometric and stereo isomers are considered. Daikin provides no guidance that any one of these compounds, or even a subgroup of these compounds, is preferred for use as a refrigerant in air conditioning systems over any other.

3. In addition to disclosing generally fluorinated propene compounds, Daikin exemplifies five fluorinated olefins: 3,3,3-trifluoro-1-propene (HFO-1243zf - see Example 1); 1,3,3,3-tetrafluoro-1-propene (HFO-1234ze – see Example 2); 1,2,2-trifluoro-1-propene (HFO-1243yc - see Example 3); 2-monofluoro-1-propene (HFO-1261yf – see Example 4); and  $\text{F}_3\text{C}-\text{CF}=\text{CH}_2$  (HFO-1234yf – see Example 5).

4. Although Daikin mentions lubrication oils generally, it does not mention or specify any particular type or class of refrigeration oil.

5. I am aware and acknowledge that our claimed invention comprises HFO-1234yf in combination with a particular lubricating oil, namely polyalkylene glycol (PAG) lubricant “in the form of a homopolymer or co-polymer consisting of 2 or more oxypropylene groups,” and which have a viscosity of “from about 10 to about 200 centistokes at about 37°C.” The claimed invention achieves two highly advantageous and unexpected results: (1) dramatically superior stability; and (2) the advantageously low toxicity of the refrigerant. These unexpected advantages are exemplified in detail below.

**STABILITY**

6. The limitations on the lubricant in the pending claims are significant because of the commercial importance of such lubricants. The vast majority of the lubricants used by original equipment manufacturers ("OEMs") in automotive air conditioning systems are PAGs consisting essentially of 2 or more oxypropylene groups and having a viscosity of from about 10 to about 200 centistokes at about 37°C. The commercial success of a refrigerant, especially in air conditioning systems, will depend to a large extent on the ability of the refrigerant molecule to exhibit a high degree of stability when used in combination with such a PAG lubricant.

7. One of the most widely used PAG lubricants at the time the present invention was made, and continuing through to the present time, is the PAG lubricant manufactured by Idemitsu Kosan and sold under the trade designation ND-8.

Certain properties of ND-8 are provided in the Table I below:

TABLE I – ND-8 PROPERTIES

Property	Viscosity, @ 40°C cSt	EO:PO Ratio	Molecular Weight
From Testing*	42.2	0:1	1058*
From US Patent 7,303,693	42.3	0:1	930

\* Based on tests of a sample of ND-8 purchased in the retail trade (molecular weight is Number Average Molecular Weight)

8. This information indicates that the PAG known as ND-8 contains essentially only oxypropylene units (as indicated by the EO:PO ratio) and has a

kinematic viscosity that would fall within the range of from about 10 to about 200 centistokes (cSt.) at about 37°C.

9. ND-8 was used to conduct stability testing in combination with several fluorinated olefins, including the preferred fluorinated olefin in accordance with the claims now pending and several of the other fluorinated olefins exemplified in Daikin. More particularly, a mixture comprising about 50% by weight of ND-8 and about 50% by weight of a selected fluorinated olefin was formed. This mixture was then subjected to several tests which are known and accepted as being indicative of the stability of such compositions. The results are provided below in Table 2:

TABLE 2

	Fluoride	TAN	Dimers
1243zf	2.8	1.6	Yes
1234yf	75	2.55	No
trans-1234ze	2166	5	No
1225yez	216	2.2	No
1261yf	160,000	85	Not possible to measure

10. The "Fluoride" reported in Table 2 was determined by first preparing the sample in accordance with ASHRE Standard 97-2007 (attached as Exhibit B) and then testing the sample using ion chromatography. This value is representative of the amount of free fluorine ions available after testing and is indicative of the stability of the combination being tested, with the higher the value the less stable the combination. As can be seen from Table 2, the HFO-1234yf/ND-8 combination has

a stability as measured by this technique which is dramatically and unexpectedly superior to that exhibited by the combination of ND-8 with the structurally similar compounds HFO-1234ze, HFO-1225yez and HFO-1261yf.

11. The total acid number, or "TAN" as reported in Table 2 was determined using ASTM D 974-06, a copy of which is attached as Exhibit C. This value indicates the TAN after testing, with the higher value the less stable the combination. As can be seen from Table 2, HFO-1234yf has a stability as measured by TAN which is also unexpectedly superior to that exhibited by the combination of this oil with the structurally similar compound HFO-1234ze.

12. The values in the column labeled "DIMER" in Table 2 were determined using gas chromatography coupled mass spectroscopy. This result indicates whether or not dimerization of the fluorinated olefin in the presence of the lubricant has occurred, which is indicative of not only the stability of the combination, but also its potential to create materials that may have a deleterious effect on the operation of an air conditioning system. As can be seen by the results reported in the "Dimers" column of Table 2, there was a substantial absence of dimers produced in the ND-8/HFO-1234yf combination. This stands in contrast to the combination of the fluorinated olefin HFO-1243zf with ND-8.

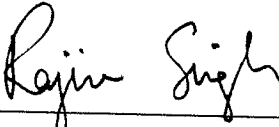
## TOXICITY

13. I am familiar with the toxicology testing reported in the first and second Rusch Declarations submitted previously in connection with this application. This

testing reveals that the tetra-fluorinated compound HFO-1234yf has toxicity properties that are substantially superior to the toxicity properties of the penta-fluorinated compound HFO-1225zc. Based on my knowledge and understanding of the state of the art at the time our invention was made, this important and significant difference was not predictable or in any way expected.

14. The toxicity properties of HFO-1234yf make it widely acceptable for use in high concentrations as a refrigerant in commercial air conditioning applications, such as automotive air conditioning systems. In contrast, HFO-1225zc has a toxicity that results in it being unacceptable for use in high concentrations as a refrigerant in commercial air conditioning applications.

15. I hereby declare that all statements made herein of my knowledge are true and that all statements made on information and belief are believed to be true and further that the statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

  
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Rajiv Singh

Dec 5, 2008  
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Date